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PACE Report No. 87-4

A STUDY OF EXPOSURE TO MOTOR GASOLINE HYDROCARBON VAPOURS AT SERVICE STATIONS (PHASE I — PILOT STUDY)

Working for a Better Environment

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PACE Report No. 87-4

Prepared for PACE by

Members of the PACE Gasoline Exposure Study Task Force

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NOTICE

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INTRODUCTION

Research findings published recently (1-4) indicated that studies exposing rats and mice to wholly vapourized unleaded gasoline produced dose-related incidences of renal damage, renal cancers and liver tumours. These studies have raised concerns over the potential hazard of gasoline vapour exposures to human health.

The PACE Health Division reviewed these findings and concluded that the interpretation of the actual risk to humans was difficult to assess in the absence of good epidemiologic data and because of the limited availability of human gasoline vapour exposure data, particularly in Canada. Therefore, the "Study of Exposure to Motor Gasoline Hydrocarbon Vapours at Service Stations" was undertaken to assess service station attendants' and self-serve customers' exposures to gasoline vapours during normal activities.

The study included three phases, namely Phase I - pilot study (preliminary), Phase II - summer study, and Phase III - winter study. The field work was carried out by four PACE member companies. A standardized sampling protocol was followed. Both area levels and personal exposure levels of gasoline vapours were measured at self-service and full-service outlets in five cities across Canada. An outside laboratory was hired for the analytical work. A consulting firm was retained to ensure that the data management and the quality assurance aspects were properly addressed.

The pilot study or phase I is the subject of this preliminary report. The purposes of the pilot study were:

(a) to verify the efficacy of the sampling method;

(b) to identify and resolve problems in the analytical method;

(c) to evaluate the performance of the selected analytical laboratory.

STUDY DESIGN

The pilot study involved:

(1) Field Sampling

The sampling took place at full-service outlets in Toronto during the period of April 14-18, 1985. The four participating member companies followed the standardized sampling protocol. Air sampling pumps calibrated at 50 cc/min. for long term samples and 1 LPM short-term samples were used with 600 mg charcoal tubes. See Appendix I for details.

The samples consisted of:

(a) three 8-hour time weighted averages (TWA's);

(b) six 15-minute short-term exposure levels (STEL's) consisting of:
- two STEL's "Regular Leaded" gasoline;
- two STEL's "Regular Unleaded" gasoline;
- two STEL's "Super Unleaded" gasoline.

(c) one blank

Each sample was taken in duplicate.

(2) Analysis

McMaster University Occupational Health Laboratory which is accredited by the American Industrial Hygiene Association, was retained for the analysis of the air samples. The analytical method developed was based on previous work undertaken by Research Triangle Institute (RTI), Raleigh, N.C., and sponsored by the American Petroleum Institute (API). Pure analytical standards for each component were obtained from Carnegie-Mellon Institute, Pittsburgh, Penn. Each front section of the charcoal tubes were analyzed twice and averaged. The back sections were analyzed once.

(3) Quality Assurance and Data Analysis

In order to ensure that the McMaster Occupational Health Laboratory was able to duplicate the analytical method developed by Research Triangle Institute, a portion of the duplicate air samples were sent to RTI for analysis. Both McMaster and RTI analyzed blind samples as follows:

(a) one charcoal tube each of a duplicate sample, for inter-laboratory comparison;
(b) both charcoal tubes of a duplicate sample, for intra-laboratory comparison; and
(c) blanks

Both front and back sections of the charcoal tubes were analyzed in duplicate by McMaster.

Concord Scientific Corporation was retained in order to oversee the data analysis and quality assurance. The parameters addressed included the determination of detection limits, sensitivity and analytical precision.

RESULTS

No particular problems were noted during sampling. Furthermore, the method proved no more cumbersome than the standard NIOSH charcoal tube method (5).

Of the 72 samples and 8 blanks originally proposed, 70 samples and 8 blanks were actually collected for the preliminary study. Four samples were discarded due to pump failure or breakage before analysis, leaving 66 samples which were analyzed and reported. Of these, two samples were deleted because of loss of duplicates. An additional two samples were deleted due to contamination.

Data analysis was therefore based on 62 samples; 24 duplicate pairs for interlaboratory analysis, and 7 duplicate pairs for intralaboratory analysis, plus 8 blanks.

McMaster found that the analytical method was able to resolve the components of interest with careful sample injection into the gas chromatograph, with two exceptions;

(1) 2-methyl-2-butene could not be resolved from the carbon disulphide peak and therefore was not reported.

(2) methylcyclohexane and 2,2-dimethylhexane could not be resolved separately and so were reported together as methylcyclohexane.

Each sample took approximately four hours for gas chromatographic analysis based on two injections (analyses) per sample. A typical chromatographic trace for a time-weighted average sample is shown in Figure 1.

The average concentration of all the short term samples by individual component analyzed is shown in Figure 2. Each point represents 42 samples and the bars on each side of the sample point indicate the range of results. Similarly, Figure 3 shows the average concentration and the range of results of all the time-weighted average samples by individual component analyzed for 20 samples.

Breakthrough of material into the backup section of charcoal was analyzed by McMaster for 21 samples. The average and range of the breakthrough ratios by component for these 24 samples are shown in Figure 4 for the 21 short-term samples and in Figure 5 for the 10 time-weighted average samples.

The component-by-component comparison of the airborne concentrations for the three duplicate sets of samples analyzed by McMaster is shown in Figures 6 and 7 for two short-term sample sets and in Figure 8 for a time-weighted sample set.

The component-by-component analysis of the airborne concentrations for the four duplicate sets of samples analyzed by RTI is shown in

Figure 9 and 10 for two short-term sample sets and in Figures 11 and 12 for the two long-term sample sets.

The interlaboratory variability is illustrated in Figure 13 which shows the mean airborne concentration, component-by-compoent-, of the 24 duplicate samples analyzed by each of the two laboratories. Only detected values were used to calculate the means of the individual compoents. Table 2 reports the number of observations used for calculating each point in Figure 13. Figure 14 is a comparison of the frequency of detection of individual gasoline components for the 24 duplicate samples analyzed by McMaster and RTI. Figure 15 illustrates a typical frequency distribution seen for the airborne concentrations of the individual components analyzed, in this case toluene.

The desorption efficiencies used by the two laboratories for the individual gasoline components analyzed are listed in Table 3.

DISCUSSION

The results of exposure to airborne concentrations of gasoline components at service stations compare well with results in the published literature (6,7,8). The distribution of the airborne concentrations of individual gasoline components appears to be lognormal, as exemplified by the distribution of the airborne concentrations of toluene shown in Figure 15. Such a distribution is expected for occupational hygiene sampling results (5).

Analysis of the breakthrough data show that the breakthrough ratios for most components did not exceed the 10% limit established by NIOSH (5). However, the very lightest component, propane, showed a consistently higher breakthrough than most other gasoline components. In order to minimize migration of propane and other components in the charcoal tube, the sample handling method was altered so that all samples taken in phases II and III would be refrigerated as soon as collected and delivered to the analytical laboratory in refrigerated condition. This slight modification decreased sample migration while still permitting comparison of the data generated in this study with other results obtained using the API sampling and analytical method.

The interlaboratory comparison shown in Figure 13 suggests that McMaster had marginally better precision than RTI. Figure 14 indicates that McMaster was able to detect individual components more often than RTI. These marginal differences in precision and detection limits are likely due to the optimization of the McMaster method with a view to obtaining the lowest possible detection limit for the PACE type of samples. Attenuation and range were modified by McMaster to give better sensitivity and McMaster used dual injections for all samples. Although there was a difference in the type of gas chromatograph used by McMaster (Hewlett-Packard 5890 Capillary Column G.C.) and RTI

(Hewlett-Packard 5880A Capillary Column G.C.), it is doubtful that this factor alone would have affected the sensitivity of the analytical method.

CONCLUSIONS AND RECOMMENDATIONS

(1) The sampling method is acceptable for the purposes of this study.

(2) To minimize migration of hydrocarbon components, future samples should be refrigerated or delivered to the analytical laboratory in this state, as soon as possible following sample collection.

(3) The analytical method was capable of adequately resolving the components of interest.

(4) McMaster Laboratories had acceptable analytical precision.

(5) It was recommended that reference charcoal tube samples of known concentration be submitted to McMaster for analysis in order to determine the laboratory's accuracy.

REFERENCES

1. MacFarland, H.N., C.E. Ulrich, C.E. Holdsworth, D.N. Kitchen, W.H. Halliwell and S.C. Blum. A Chronic Inhalation Study with Unleaded Gasoline Vapor. J. Amer. Coll. Toxicol. 3 (4):231-248 (1984).

2. Carpenter, C.P., E.R. Kinkead, D.L. Geary, Jr., L.J. Sullivan and J.M. King. Petroleum Hydrocarbon Toxocity Studies. 111. Animal and Human Response to Vapors of Stoddard Solvent. Toxicol. Appl. Pharmacol. 32:282-297 (1975).

3. Carpenter, C.P., E.R. Kinkead, D.L. Geary, Jr., L.J. Sullivan and J.M. King. Petroleum Hydrocarbon Toxocity Studies. VI. Animal and Human Response to Vapors of 60 Solvent. Toxicol. Appl. Pharmacol. 34:374-394 (1975).

4. Carpenter, C.P., D.L. Geary, Jr., R.C. Myers, D.J. Nachreiner, L.J. Sullivan and J.M. King. Petroleum Hydrocarbon Toxicity Studies. XV. Animal Response to Vapors of High Naphthenic Solvent. Toxicol. Appl. Pharmacol. 41:251-260 (1977).

5. NIOSH.1984. NIOSH Manual of Analytical Methods. Method 1500. DHHS(NIOSH) Publication No. 84-100 U.S. Government Printing Office, Washington, D.C.

6. McDermott, H.J. and G.A. Vos. Service Station Attendants' Exposure to Benzene and Gasoline Vapors. Am. Ind. Hyg. Assoc. J. 40:315-321 (1979).

7. Halder, C.A., and G.S. Van Gorp, N.S. Hatoum and T.M. Warne. Gasoline Vapour Exposures. Part I. Characterization of Workplace Exposures. Amer. Ind. Hyg. Assoc. J. 47:164-1972 (1986).

8. Kearney, C.A. and D.B. Dunham. Gasoline Vapor Exposures at a High Volume Service Station. Amer. Ind. Hyg. Assoc. J. 47:535-539 (1986).

TABLE 1

GASOLINE VAPOUR COMPONENTS

COMPONENT NO.	CHEMICAL NAME	CAS NUMBER	CARBON NUMBER	HYDROCARBON GROUP
1	Propane	74-98-6	3	n-paraffins
2	Isobutane	75-28-5	4	isoparaffins
3	1-Butene	106-98-9	4	olefins
4	n-Butane	106-97-8	4	n-paraffins
5	Trans-2-butene	624-64-6	4	olefins
6	Cis-2-butene	107-01-7	4	olefins
7	3-Methyl-1-butene	563-45-1	5	olefins
8	Isopentane	109-68-2	5	isoparaffins
9	1-Pentene	109-67-1	5	olefins
10	2-Methyl-1-butene	563-46-2	5	olefins
11	n-Pentane	109-66-0	5	n-paraffins
12	Trans-2-pentene	646-04-8	5	olefins
13	2-Methyl-2-butene	513-35-9	5	olefins
14	Cyclopentane	287-92-3	5	cycloparaffins
15	2,3-Dimethylbutane	79-29-8	6	isoparaffins
16	2-Methylpentane	107-83-5	6	isoparaffins
17	3-Methylpentane	96-14-0	6	isoparaffins
18	1-Hexene	592-41-6	6	olefins
19	n-Hexane	110-54-3	6	n-paraffins
20	Trans-3-methyl-2-pentene	616-12-6	6	olefins
21	2,2-Dimethylpentane	590-35-2	7	isoparaffins
22	Methylcyclopentane	96-37-7	6	cycloparaffins
23	2,4-Dimethylpentane	108-08-7	7	isoparaffins
24	2,2,3-Trimethylbutane	464-06-2	7	isoparaffins
25	Cis-4,4-dimethylpentene	762-62-9	7	olefins
26	Benzene	71-43-2	6	aromatics
27	3,3-Dimethylpentane	562-49-2	7	isoparaffins
28	Cyclohexane	110-82-7	6	cycloparaffins
29	2-Methylhexane	591-76-4	7	isoparaffins
30	2,3-Dimethylpentane	565-59-3	7	isoparaffins
31	3-Methylhexane	589-34-4	7	isoparaffins
32	3-Ethylpentane	617-78-7	7	isoparaffins
33	1-Heptene	592-76-7	7	olefins
34	2,2,4-Trimethylpentane	540-84-1	8	isoparaffins
35	n-Heptane	142-82-5	7	n-paraffins
36	Methylcyclohexane and	108-87-2	7,8	cycloparaffins
	2,2-Dimethylhexane	590-73-8		isoparaffins
37	2,5-Dimethylhexane	592-13-2	8	isoparaffins
38	2,4-Dimethylhexane	589-43-5	8	isoparaffins
39	3,3-Dimethylhexane	563-16-6	8	isoparaffins
40	2,3,4-Trimethylpentane	565-75-3	8	isoparaffins
41	Toluene	108-88-3	7	aromatics
42	2-Methylheptane	592-27-8	8	isoparaffins
43	3,4-Dimethylhexane	583-48-2	8	isoparaffins
44	3-Methylheptane	589-81-1	8	isoparaffins
45	2,2,5-Trimethylhexane	3522-94-9	9	isoparaffins
46	n-Octane	111-65-9	8	n-paraffins
47	Ethylbenzene	100-41-4	8	aromatics
48	m-Xylene	1330-20-7	8	aromatics
49	p-Xylene	1330-20-7	8	aromatics
50	o-Xylene	1330-20-7	8	aromatics
51	n-Nonane	111-84-2	9	n-paraffins
52	Isopropylbenzene	98-82-8	9	aromatics
53	Ethyltoluene	611-14-3	9	aromatics
54	1,3,5-Trimethylbenzene	108-67-8	9	aromatics
55	n-Decane	124-18-5	10	n-paraffins
56	Gasoline as Total Hydrocarbons (THC)		-	-

TABLE 2

NUMBER OF OBSERVATIONS USED CALCULATING EACH POINT FOR FIG. 13

	McMaster	R.T.I.
Propane	23	19
Isobutane	24	24
1-Butene	24	10
n-Butane	24	24
Trans-2-butene	22	24
Cis-2-butene	23	24
3-Methyl-1-butene	23	8
Isopentane	24	23
1-Pentene	21	11
2-Methyl-1-butene	16	2
n-Pentane	24	24
Trans-2-pentene	14	9
2-Methyl-2-butene	0	13
Cyclopentane	24	6
2.3-Dimethylbutane	24	15
2-Methylpentane	24	23
3-Methylpentane	24	23
1-Hexene	24	7
n-Hexane	24	24
Trans-3-methyl-2-pentene	21	7
2,2-Dimethylpentane	17	1
Methylcyclopentane	24	20
2,4-Dimethylpentane	24	10
2,2,3-Trimethylbutane	13	0
Cis-4,4-dimethylpentene	9	0
Benzene	24	23
3,3-Dimethylpentane	17	1
Cyclohexane	24	7
2-Methylhexane	24	17
2,3-Dimethylpentane	24	13
3-Methylhexane	24	17
3-Ethylpentane	24	8
1-Heptene	8	1
2,2,4-Trimethylpentane	22	13
n-Heptane	21	15
Methylcyclohexane	24	3
2,5-Dimethylhexane	19	0
2,4-Dimethylhexane	18	5
3,3-Dimethylhexane	16	0
2,3,4-Trimethylpentane	24	4
Toluene	24	22
2-Methylheptane	23	6
3,4-Dimethylhexane	8	0
3-Methylheptane	24	6
2,2,5-Trimethylhexane	11	1
n-Octane	24	3
Ethylbenzene	24	4
m-Xylene	24	0
p-Xylene	1	14
o-Xylene	24	7
n-Nonane	15	2
Isopropylbenzene	10	0
Ethyltoluene	22	4
1,3,5-Trimethylbenzene	1	14
n-Decane	11	5

TABLE 3: DESORPTION EFFICIENCIES BY COMPONENT

COMPONENT NO.	COMPOUND	DESORPTION EFFICIENCY
1	Propane	1.000
2	Isobutane	1.000
3	1-Butene	1.000
4	n-Butane	1.000
5	Trans-2-butene	1.000
6	Cis-2-butene	1.000
7	3-Methyl-1-butene	1.000
8	Isopentane	1.000
9	1-Pentene	1.000
10	2-Methyl-1-butene	1.000
11	n-Pentane	1.000
12	Trans-2-pentene	1.000
13	2-Methyl-2-butene	
14	Cyclopentane	1.000
15	2,3-Dimethylbutane	1.000
16	2-Methylpentane	1.000
17	3-Methylpentane	1.000
18	1-Hexene	1.000
19	n-Hexane	1.000
20	Trans-3-methyl-2-pentene	1.000
21	2,2-Dimethylpentane	0.963
22	Methylcyclopentane	1.000
23	2,4-Dimethylpentane	1.000
24	2,2,3-Trimethylbutane	0.981
25	Cis-4,4-Dimethylpentene	1.000
26	Benzene	0.930
27	3,3-Dimethylpentane	1.000
28	Cyclohexane	0.770
29	2-Methylhexane	1.000
30	2,3-Dimethylpentane	1.000
31	3-Methylhexane	0.971
32	3-Ethylpentane	1.000
33	1-Heptene	0.966
34	2,2,4-Trimethylpentane	0.933
35	n-Heptane	0.952
36	Methylcyclohexane and 2,2-Dimethylhexane	1.000
37	2,5-Dimethylhexane	0.960
38	2,4-Dimethylhexane	0.965
39	3,3-Dimethylhexane	1.000
40	2,3,4-Trimethylpentane	1.000
41	Toluene	0.823
42	2-Methylheptane	0.945
43	3,4-Dimethylhexane	0.945
44	3-Methylheptane	1.000
45	2,2,5-Trimethylhexane	0.950
46	n-Octane	0.948
47	Ethylbenzene	0.916
48	m-Xylene	0.885
49	p-Xylene	0.853
50	o-Xylene	0.798
51	n-Nonane	1.000
52	Isopropylbenzene	0.964
53	Ethyltoluene	1.000
54	1,3,5-Trimethylbenzene	0.912
55	n-Decane	1.000

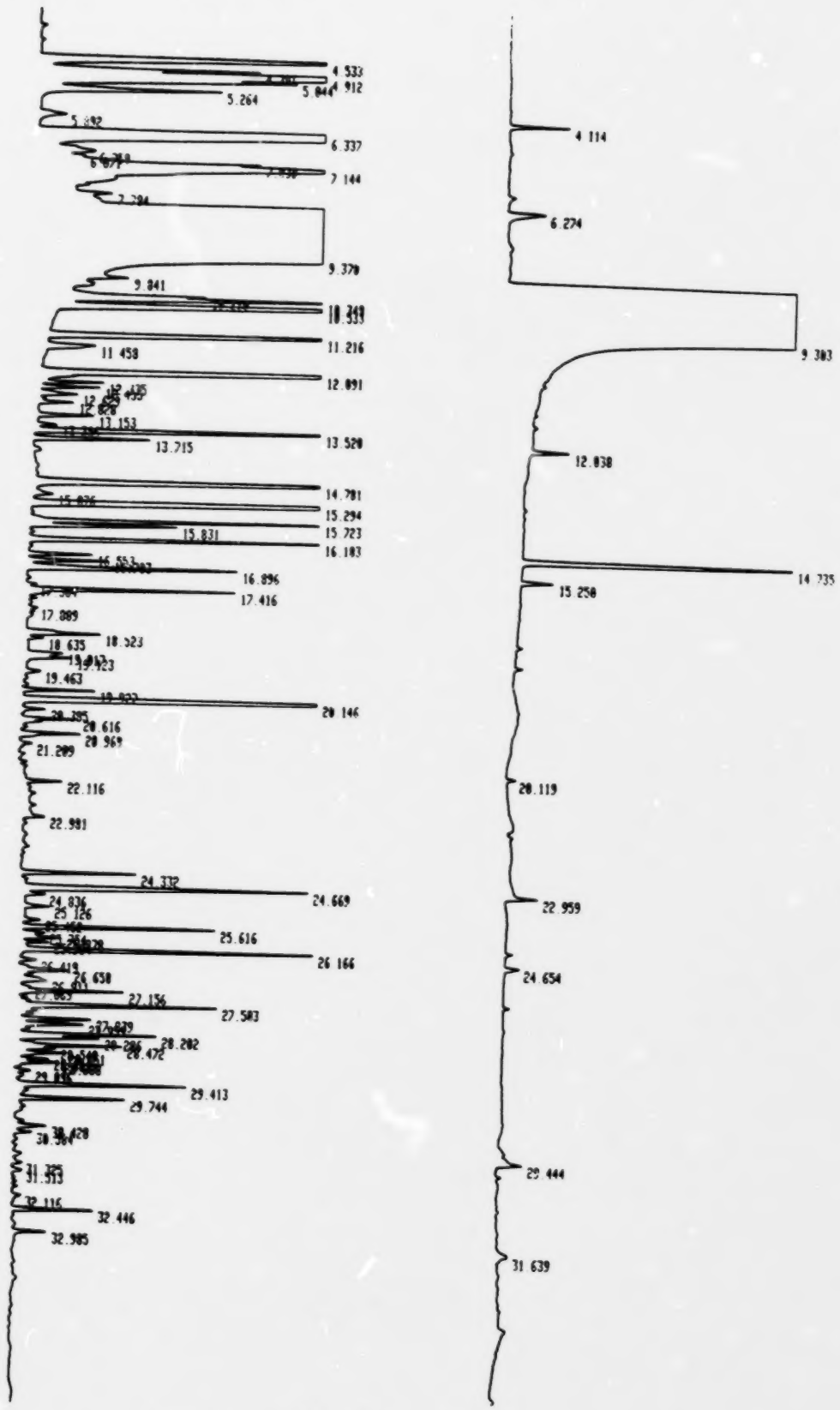


Figure 1 - Sample Gas Chromatographic Analysis of Gasoline

FIG. 2. AIRBORNE CONCENTRATION BY COMPONENT FOR SHORT TERM SAMPLES

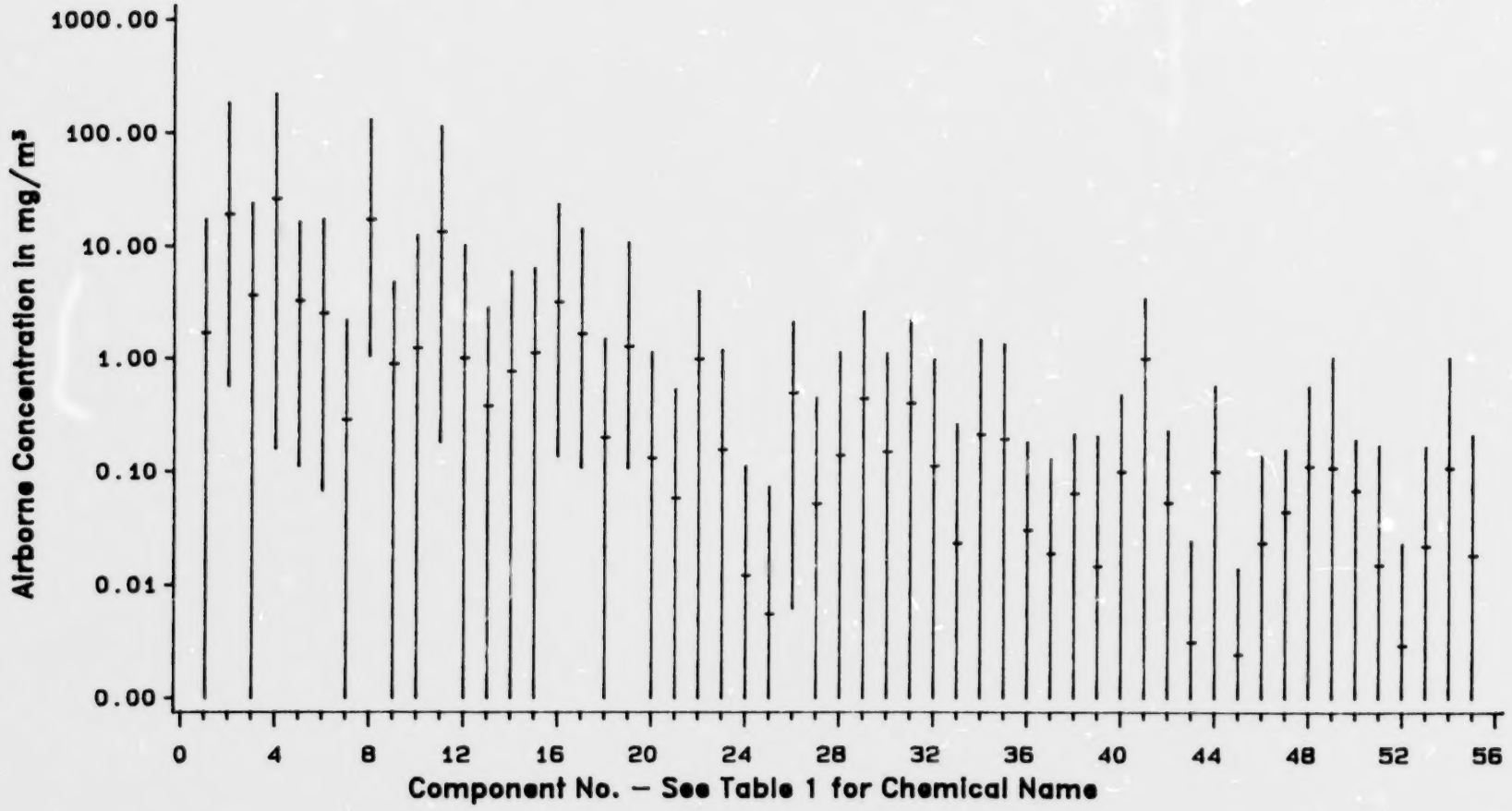


FIG. 3. AIRBORNE CONCENTRATION BY COMPONENT FOR TIME WEIGHTED AVERAGE SAMPLES

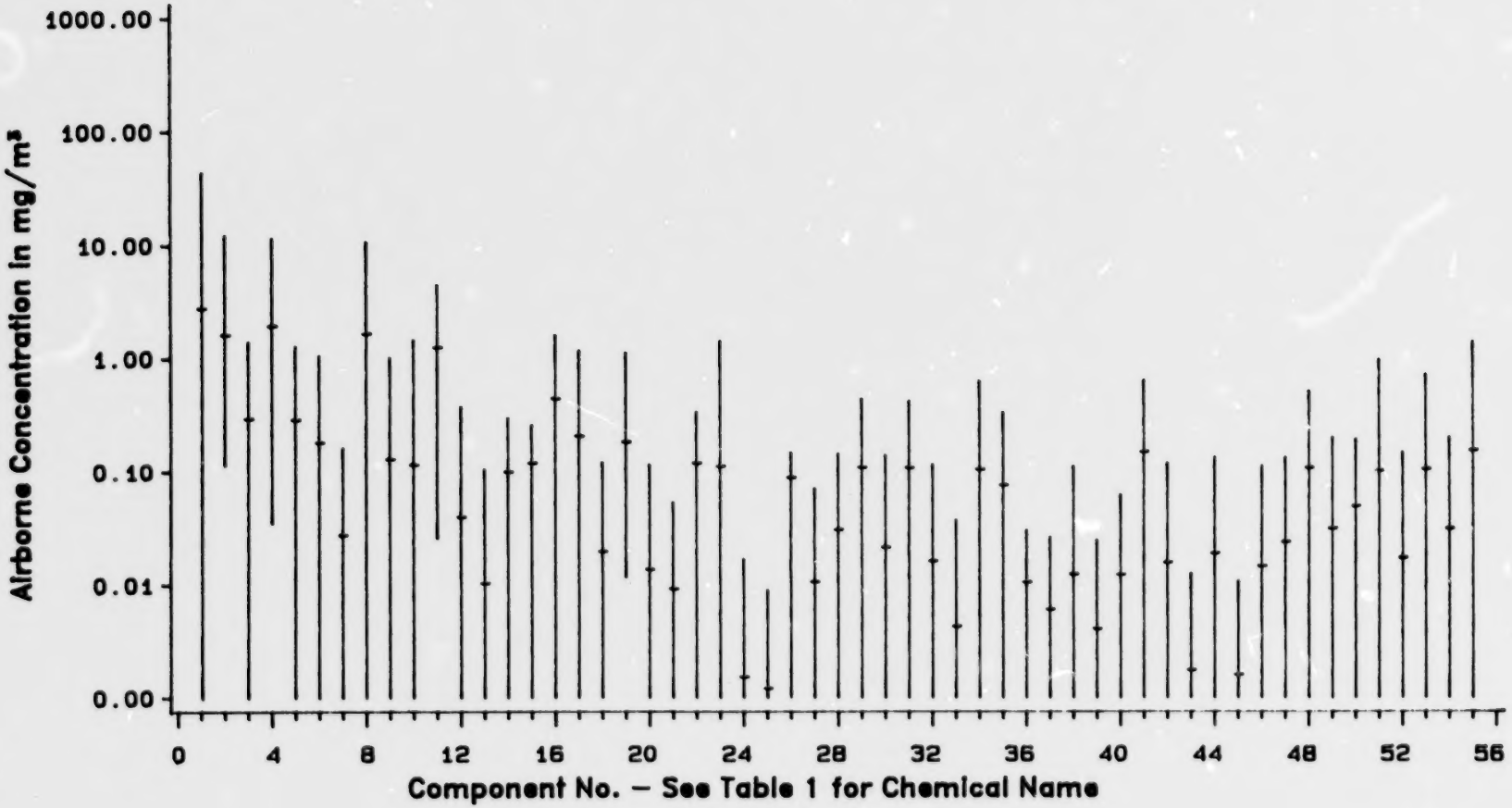


FIG. 4. BREAKTHROUGH RATIO BY COMPONENT FOR SHORT TERM SAMPLES ANALYSED BY MCMASTER UNIVERITY

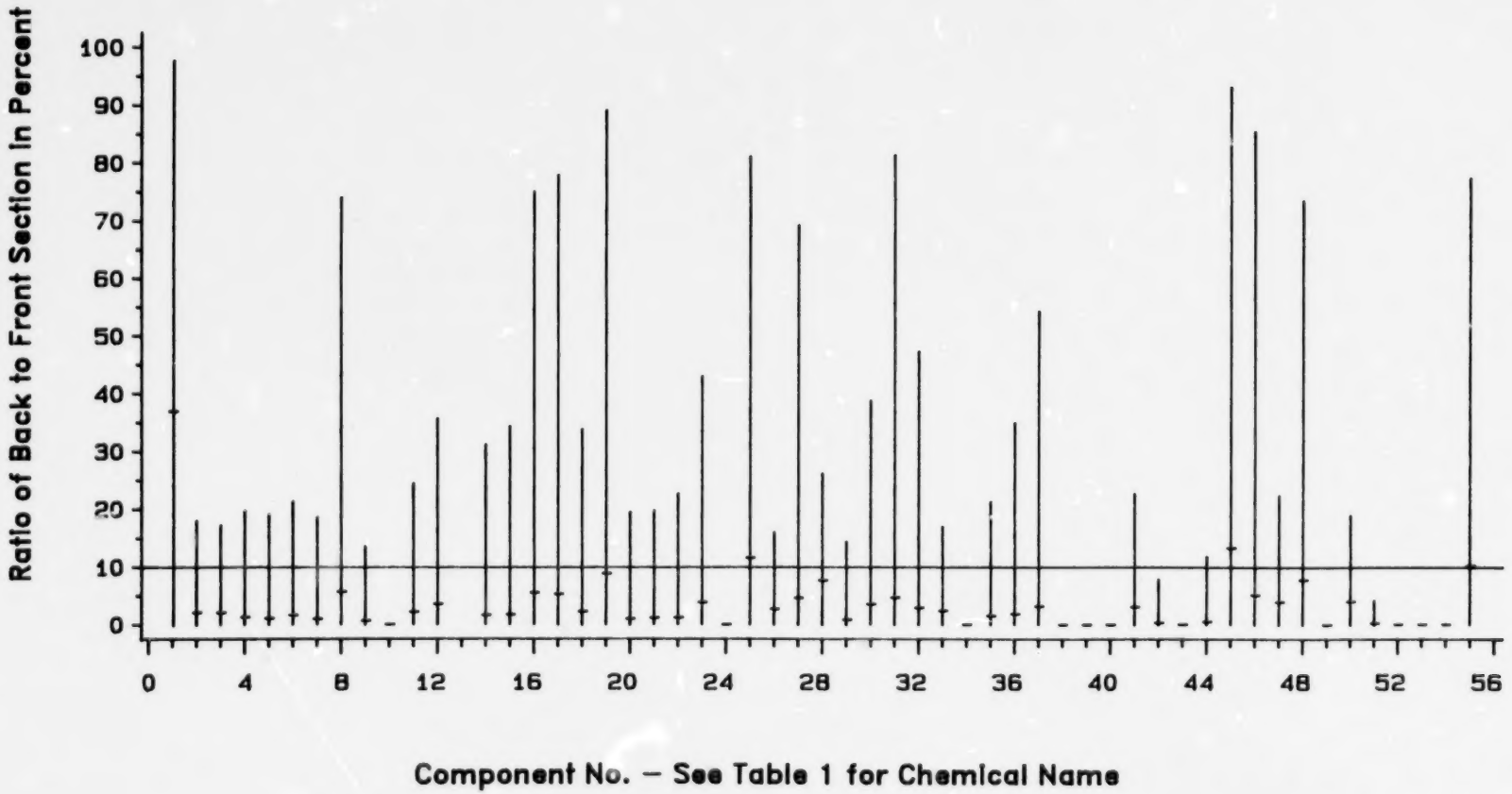


FIG. 5. BREAKTHROUGH RATIO BY COMPONENT FOR TIME WEIGHTED AVERAGE SAMPLES ANALYSED BY MCMASTER UNIVERITY

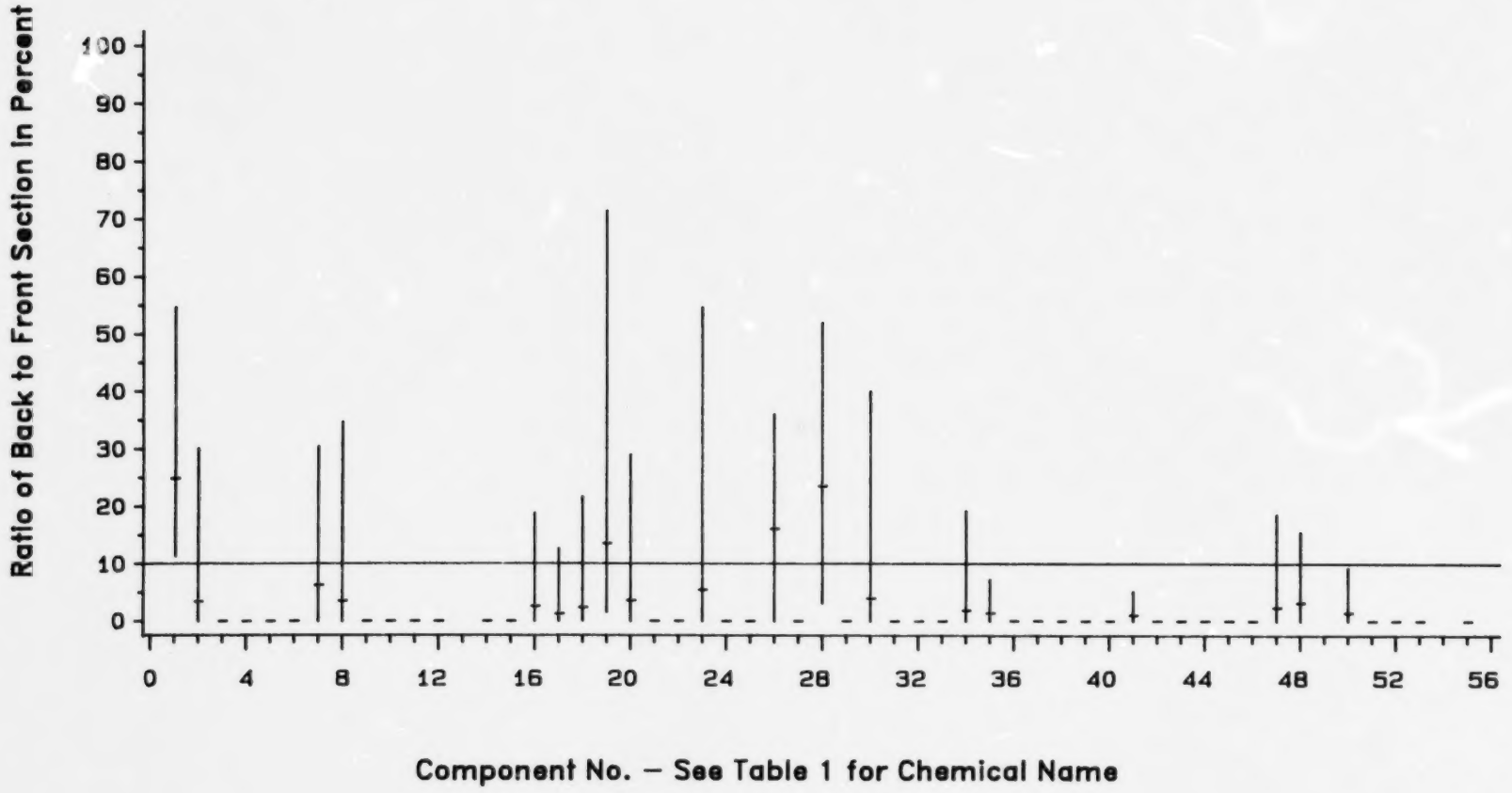


FIG. 6. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY McMASTER UNIVERSITY

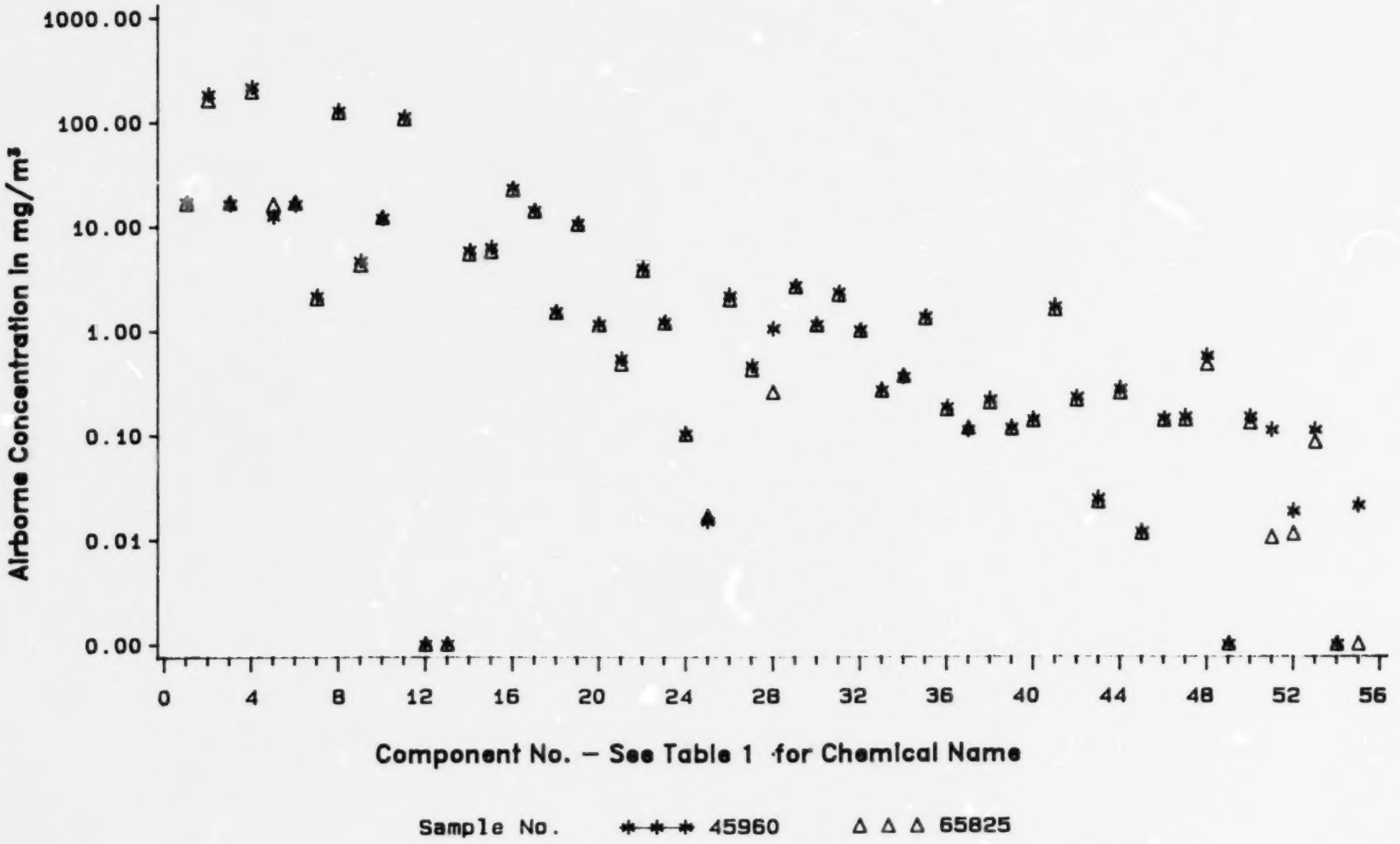


FIG. 7. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY McMASTER UNIVERSITY

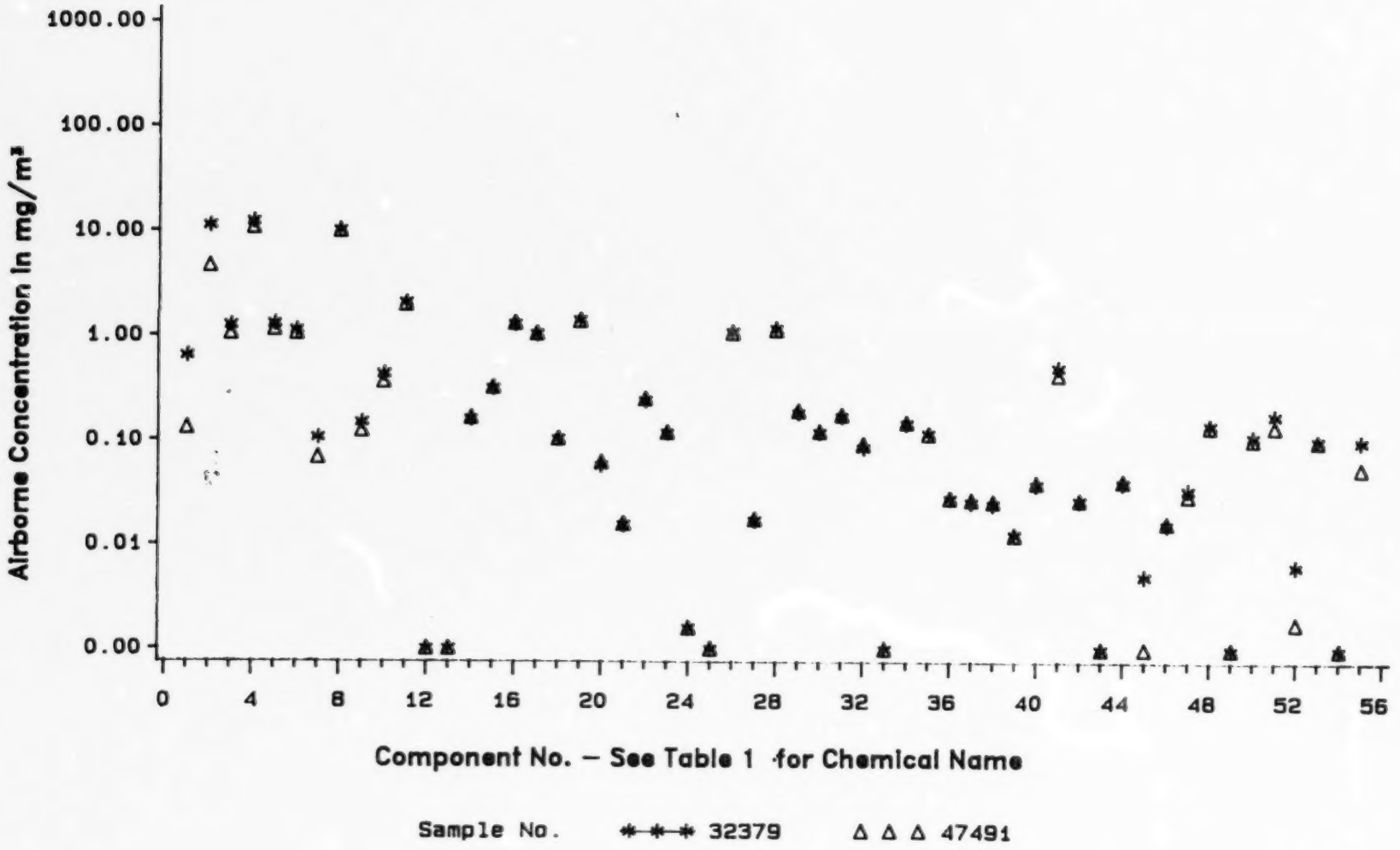


FIG. 8. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY McMASTER UNIVERSITY

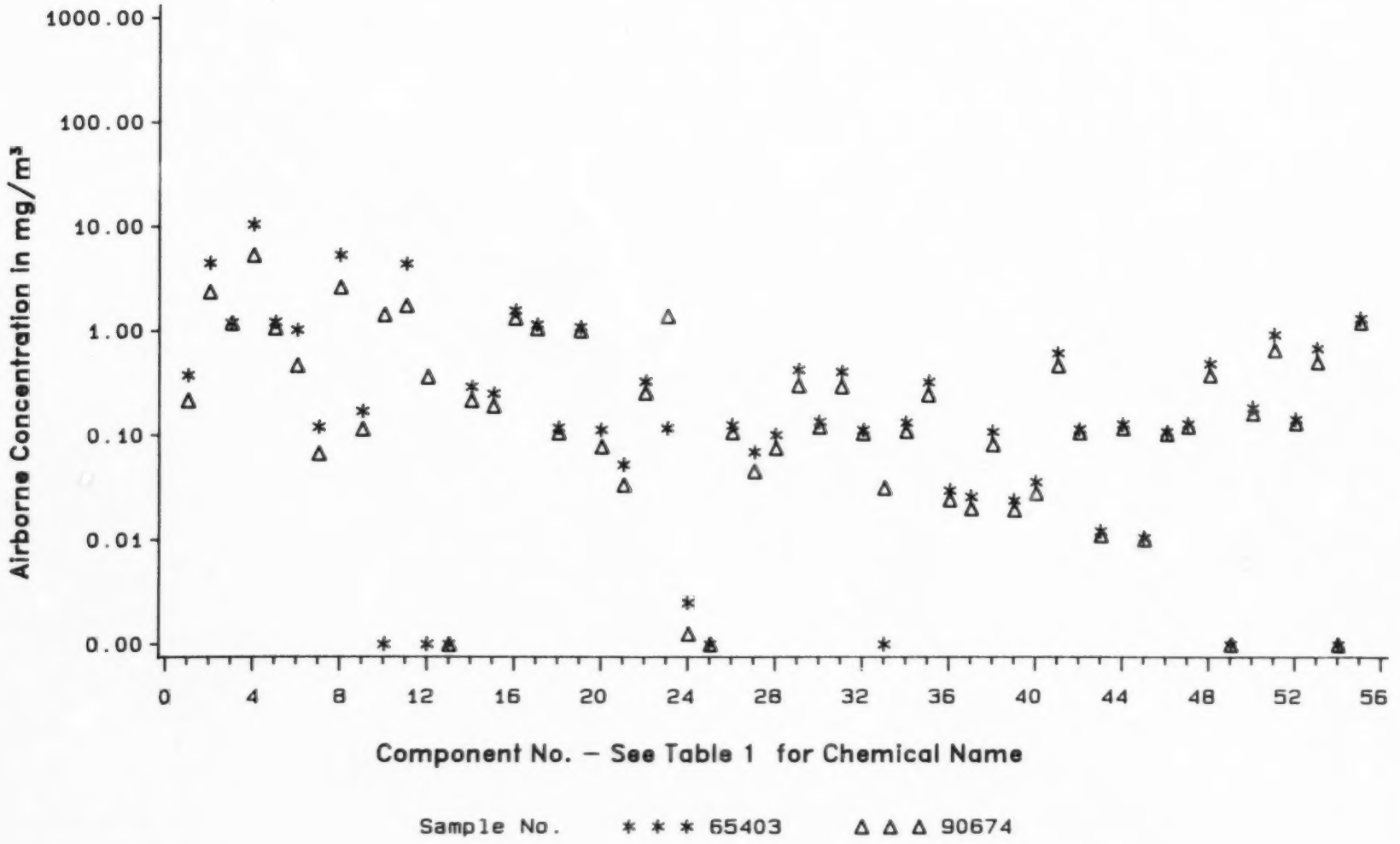


FIG. 9. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY RESEARCH TRIANGLE INSTITUTE

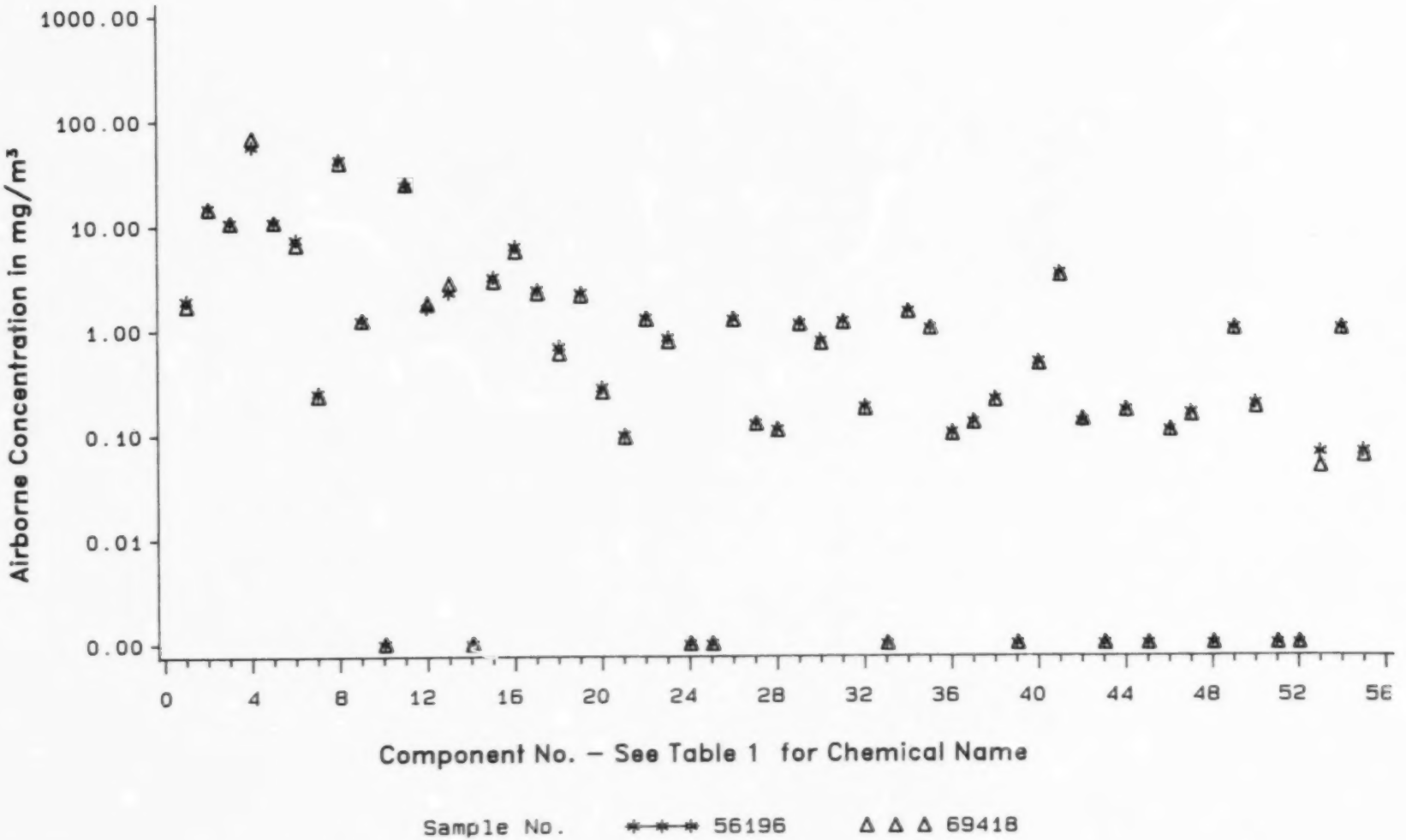


FIG. 10. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY RESEARCH TRIANGLE INSTITUTE

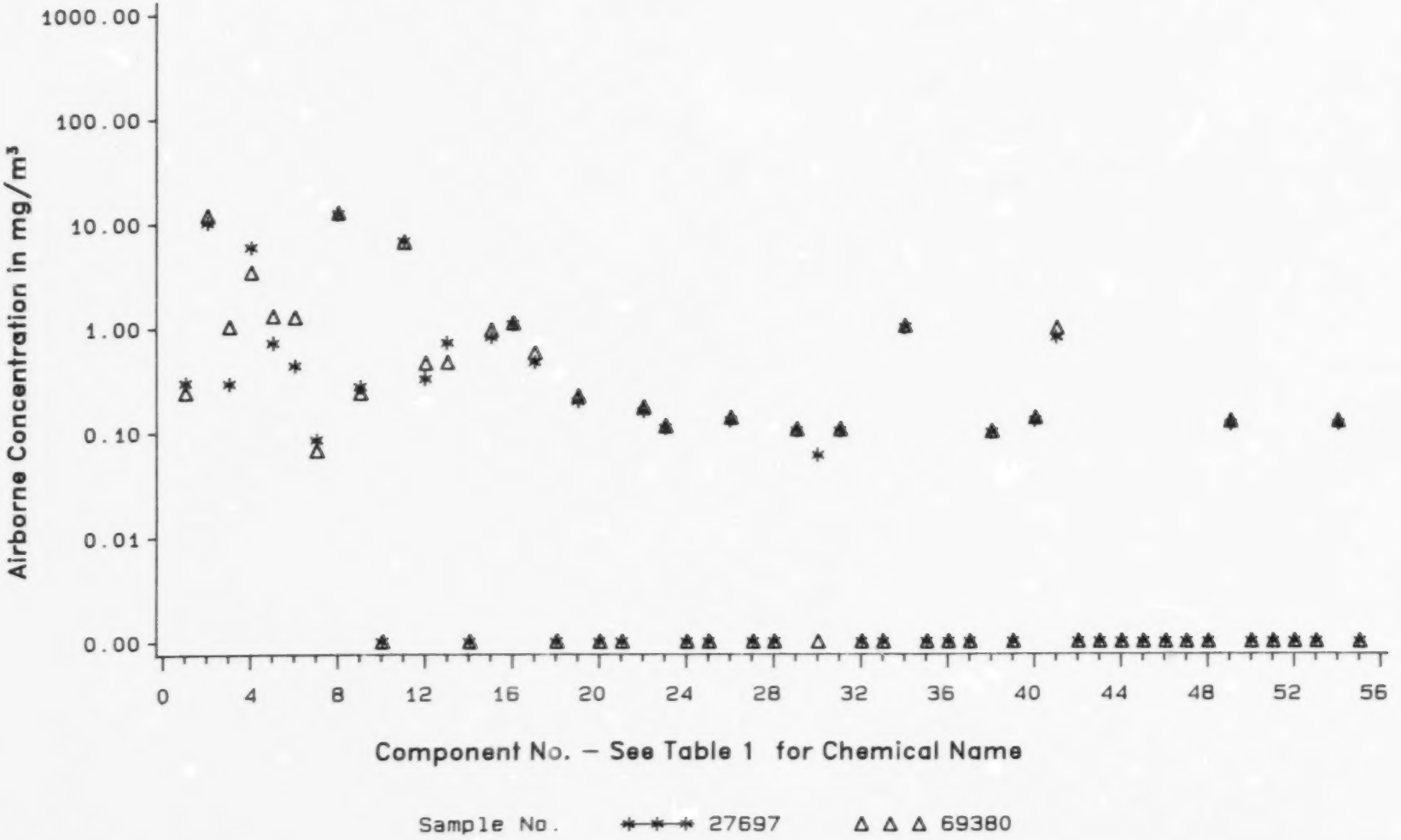


FIG. 11. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY RESEARCH TRIANGLE INSTITUTE

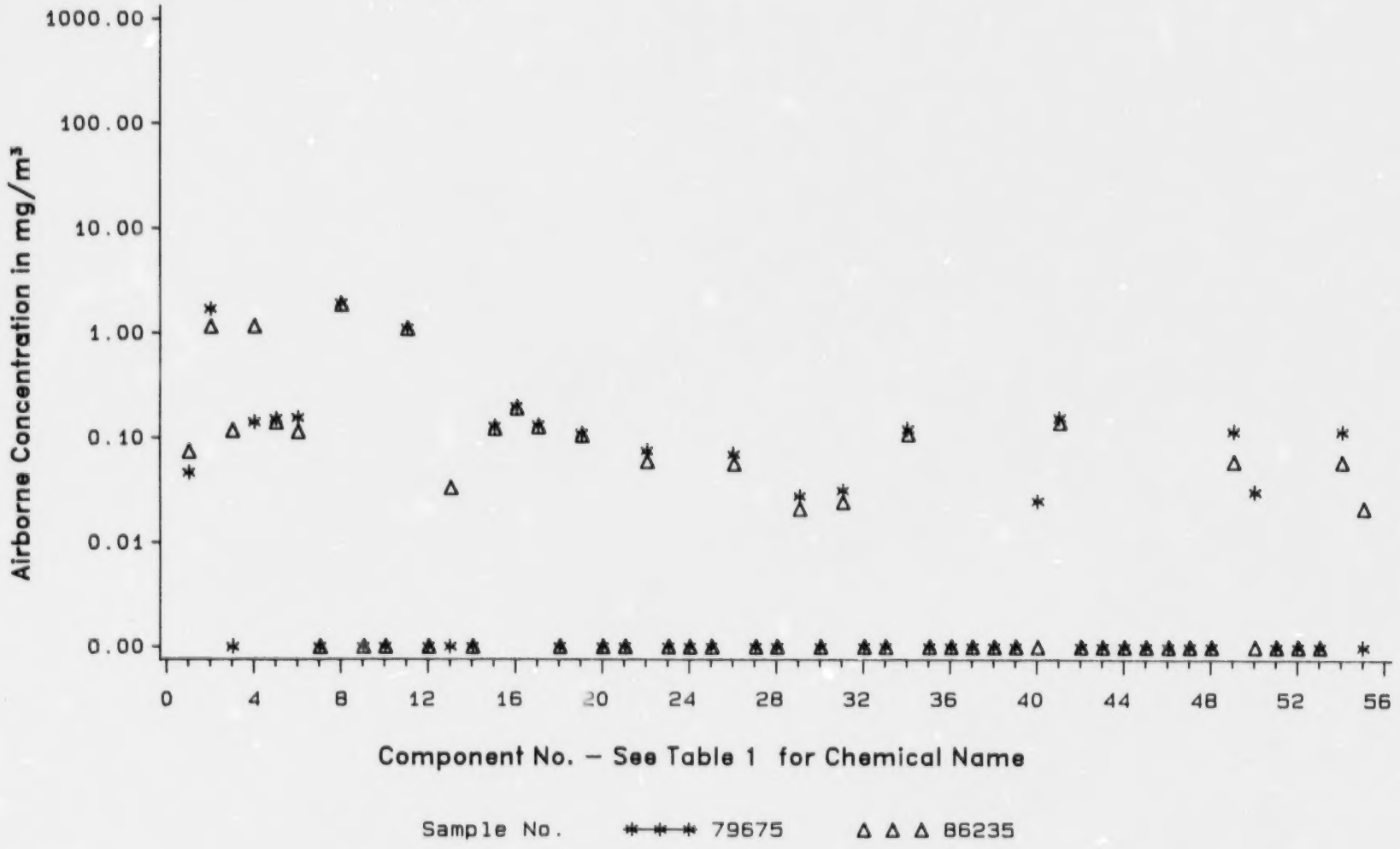


FIG. 12. INTRALABORATORY COMPARISON BETWEEN DUPLICATE SAMPLES ANALYSED BY RESEARCH TRIANGLE INSTITUTE

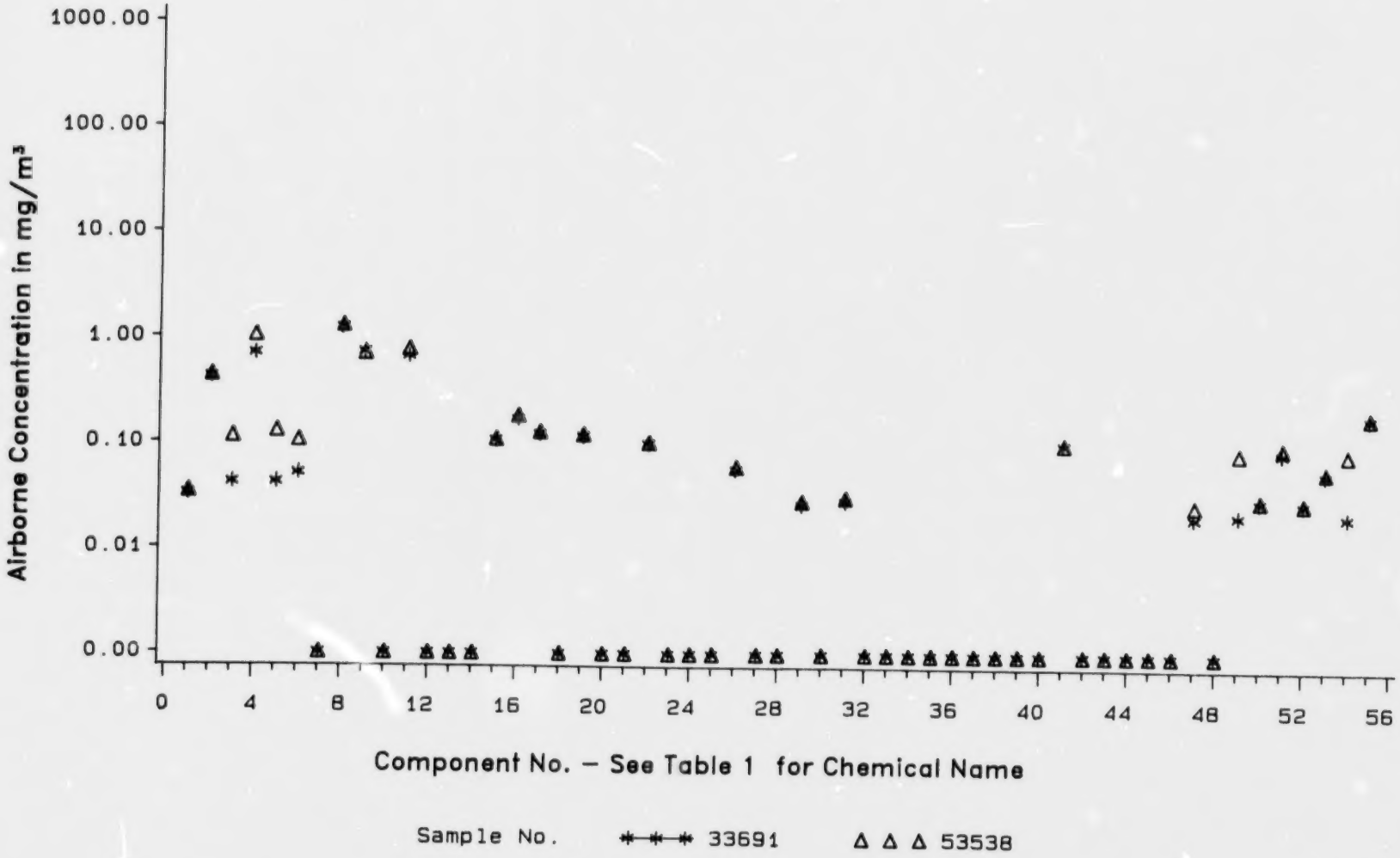


FIG. 13. INTERLABORATORY COMPARISON OF MEAN AIRBORNE CONCENTRATION BY COMPONENT

(Note: These means are calculated for detected values only)

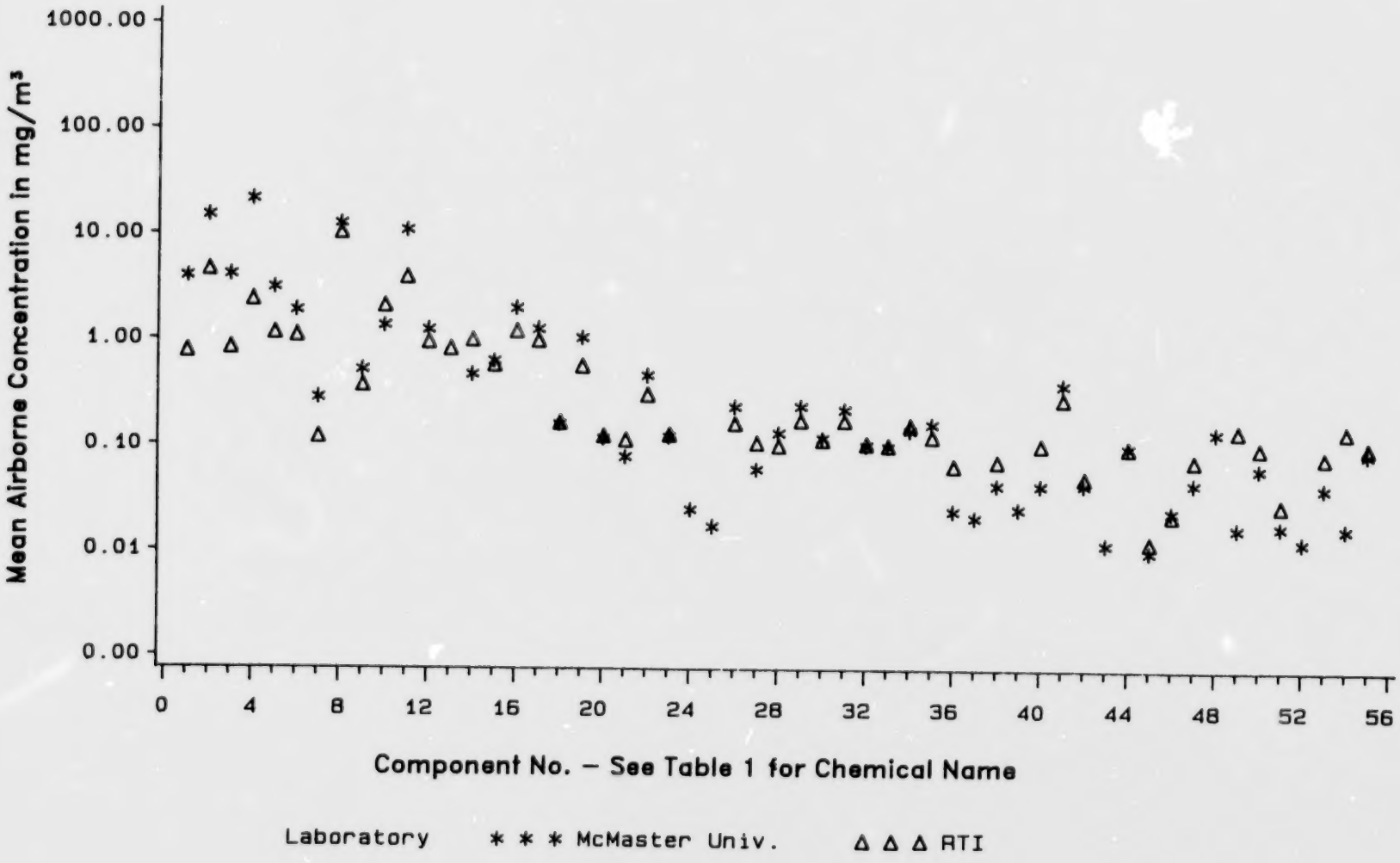


FIG. 14. FREQUENCY OF COMPONENT DETECTED BY LABORATORY FOR 24 DUPLICATE SAMPLES

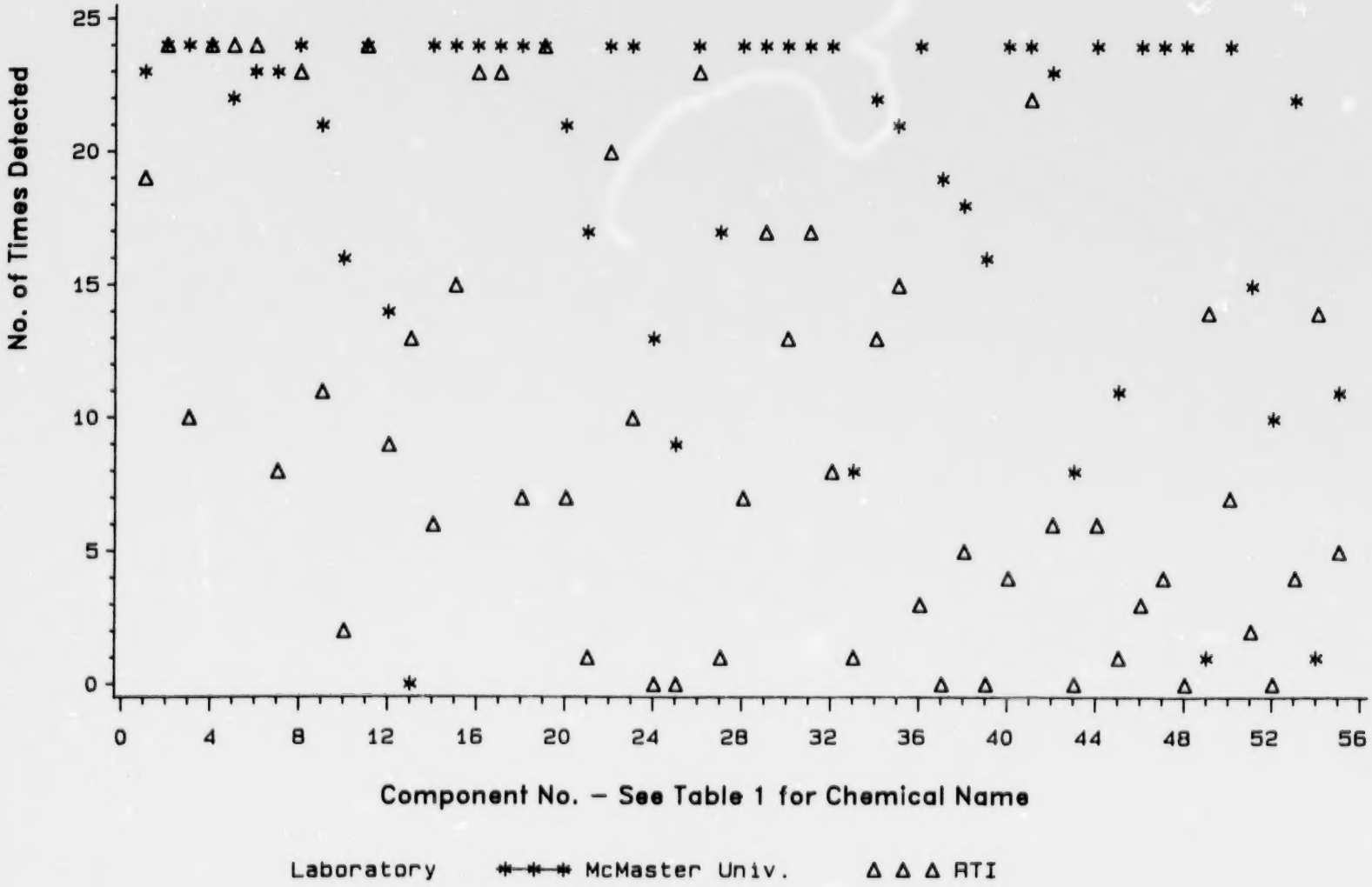
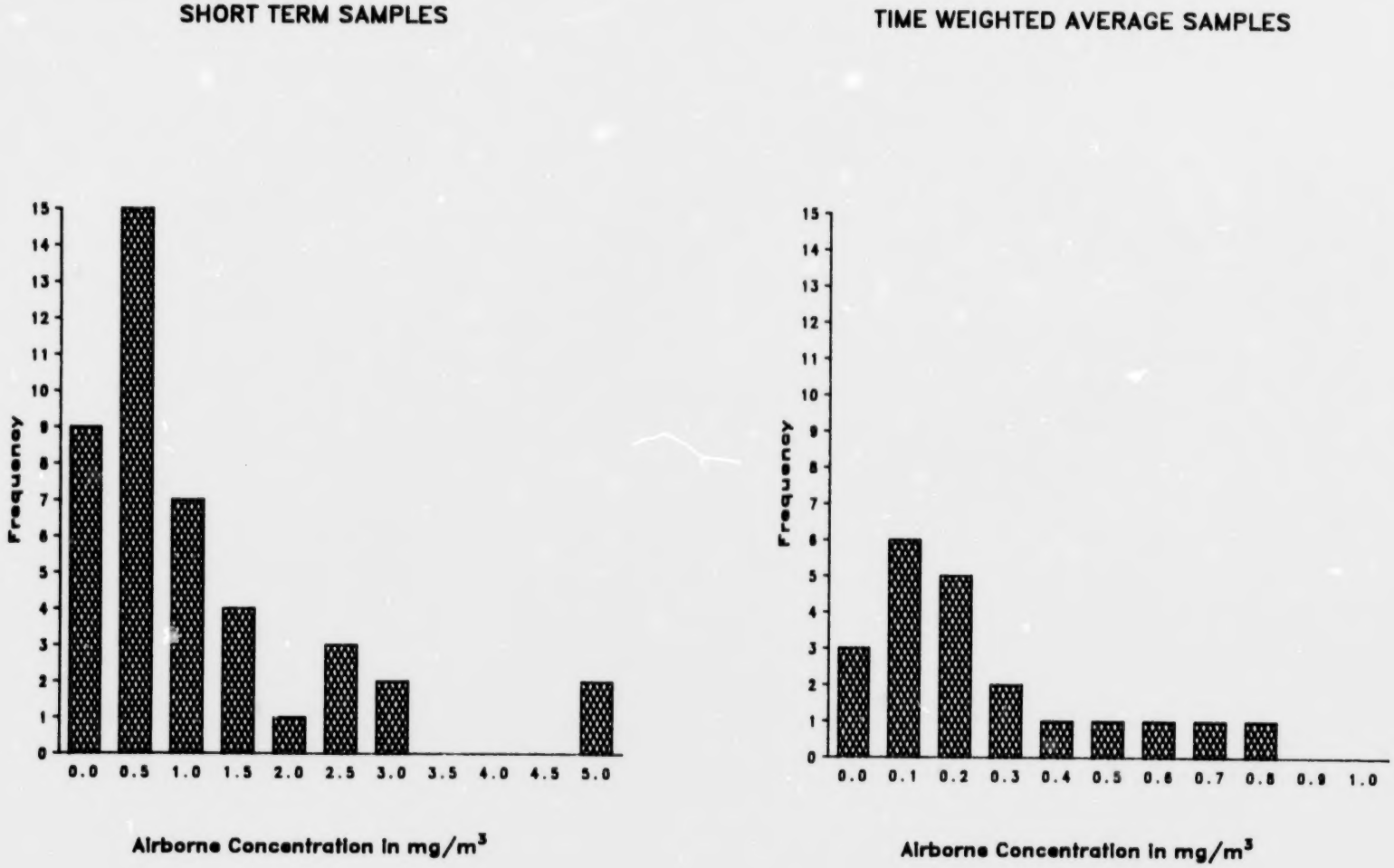


FIG. 15. DISTRIBUTION OF AIRBORNE CONCENTRATION FOR TOLUENE


SHORT TERM SAMPLES
Frequency
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
Airborne Concentration in mg/m3
TIME WEIGHTED AVERAGE SAMPLES
Frequency
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Airborne Concentration in mg/m3

APPENDIX I

STUDY OF EXPOSURE TO MOTOR GASOLINE HYDROCARBONS

AIR SAMPLING METHOD

(PHASE I - PILOT STUDY)

PRINCIPLE

Air possibly containing gasoline vapours was drawn at a specified flow rate for a known durate through an activated charcoal tube. The various gasoline components absorbed on the charcoal were desorbed with carbon disulfide and analyzed by capillary column gas chromatography.

A. AIR SAMPLING

1. Equipment

All equipment was supplied by participating member companies with the exception of charcoal tubes, sealing caps, and bulk sample bottles which were provided through the study taskforce.

The sampling train used to obtain an air sample containing the gasoline vapours included the following components and satisfied the stated criteria:

(a) A battery operated portable pump

- capable of delivering for 8 hours or full shift 50 cc/min. with a large charcoal tube (600 mg) in the sampling train, and up to 1000 cc/min. with a large charcoal tube for a period of 15 minutes.

- intrinsically safe i.e. meets the National Electrical Code Class 1, Divison 1, Group D as a minimum.

(b) A charcoal tube, large size (i.e. 400 mg front, 200 mg back). Identified by a random number generated by Concord Scientific Corp.

(c) A charcoal tube holder of appropriate size, which

included a clip for attachment to clothing, and an adaptor for flexible tubing to ensure a leak proof fit.

(d) Tygon tubing of sufficient length and appropriate wall thickness to prevent collapse when air is drawn through and with appropriate inner diameter to provide a leak proof fit to the tube holder and to the inlet port of the portable pump.

2. SAMPLING PROCEDURE

(a) Before sampling:

- The pump battery pack was fully charged, according to the manufacturer's instructions.

- The pump was calibrated to the specified flow rate with the appropriate size charcoal tube in line using a primary standard e.g. a bubble meter, at the start and the end of each sampling day. The pump was allowed to run for at least 5 minutes before the first calibration. For long-term samples, minimum of 7 hours, the flow rate was about 50 cc/minute using large (600 mg) size charcoal tube. For short-term samples, minimum 10 minutes and maximum 15 minutes, the flowrate was 1000 cc/minute using a large (600 mg) size charcoal tube. The established flow rate was an average of three readings taken using the primary standard.

(b) Sampling:

- The duplicate samples taken by the four participating companies were:

  three (3) 8-hr. TWA's

  six (6) 15 min. STEL's made up of:

  2 Regular Leaded
  2 Regular Unleaded
  2 Super Unleaded

  1 blank

The following procedures were used to assemble the sampling train:

- the charcoal tube was broken open with a minimum 2mm opening;

- the tube was inserted into the holder with the arrow

on charcoal tube pointing towards the pump;

- one end of the tubing was attached to holder and the other end to the inlet port of the pump;

- The pump was attached to the person and the tube holder was clipped in a vertical position near to the breathing zone, ensuring that the equipment did not interfere with the person's normal work activities.

- The pump was switched on noting the start time and/or start count.

- The required information was recorded on the "Industrial Hygiene Sampling Data Sheet", attached.

- Each set of samples included one blank charcoal tube obtained from the same batch of charcoal tubes and handled in the same manner as the sample tube (break, seal, transport) except that no air was drawn through it.

- If attendant left the site, the pump was removed, turned off, and the time recorded.

- During the sampling interval the sampling train was periodically checked, to ensure that it was functioning properly.

- For short-term samples the sampling pump was turned on when the gas tank cap was opened and turned off when the gask tank cap was replaced. The charcoal tube was capped between individual fill ups.

- Recorded pertinent information such as, station throughput, work habits, exceptional activities, etc. on the sampling data sheet.

(c) Termination of Sampling

- The pump was switched off and the stop time and/or end count recorded.

- The sampling train was then removed from the person.

- The charcoal tube was removed from the holder and both ends were capped using the supplied caps.

- The tube was stored in a refrigerator and left there during the entire week of sampling.

- The sampling pump was recalibrated.

- The tubes were shipped to the analytical lab.

(d) Environmental Data

- T, P, and RH were obtained from local weather office (uncorrected BP levels). Wind speed was measured at the station.

PACE GASOLINE EXPOSURE STUDY

INDUSTRIAL HYGIENE SAMPLING DATA SHEET

SAMPLE NUMBER: _____

DUPLICATE OF: _____

DATE (Yr/Mth/day): _____

1. LOCATION: ☐ Hfx. ☐ Mtl. ☐ Tor. ☐ Cgy. ☐ Vcr.
2. TYPE OF OPERATION: ☐ Full Serve ☐ Self-Serve
3. JOB FUNCTION TITLE: ☐ Pumper ☐ Kiosk Operator
4. JOB ACTIVITY: ☐ Pumping Gas ☐ Tank Dip ☐ Fuel Sample
   ☐ Attending Kiosk ☐ Mechanical Work ☐ Windshield
   ☐ Spill Clean-Up
5. TYPE OF SAMPLE:
   ☐ Long Term ☐ Short Term ☐ Area ☐ Bulk
   ☐ Reg Pb ☐ North
   ☐ Reg ☐ South
   ☐ Super ☐ East
   ☐ West
6. RELATIVE HUMIDITY: _____ %
7. AVERAGE TEMPERATURE: _____ °C
8. BAROMETRIC PRESSURE: _____ KPa
9. WIND SPEED (ft/sec): ☐ a.m. ☐ p.m. ☐ mid-day
10. WIND DIRECTION(from): ☐ a.m. ☐ p.m. ☐ mid-day
11. WORKER TO SOURCE: ☐ Upwind ☐ Downwind ☐ Variable
12. KIOSK LOCATION: ☐ Centre ☐ Side _____ Distance (m)
13. SMOKING: ☐ Yes ☐ No
14. OTHER MATERIALS (check only if filled): ☐ Propane
    ☐ Diesel ☐ Gasohol
15. SERVICE STATION TOTAL THROUGHPUT (litres) _____

Flow Rate Start	End	Avg. Flow Rate

Start Count	End	Total Net Count

Start Vol/Stroke	End	Avg. Vol/Stroke

START TIME _____ STOP TIME _____ TOTAL TIME _____

TOTAL VOLUME OF AIR SAMPLES (Litres): _____

COMMENTS, WORK TASK DETAILS
REMARKS, DIAGRAM, ETC.

SAMPLE MEDIA: 600 mg Charcoal Tube

CALIBRATION METHOD: Bubble Meter

SAMPLING EQUIP.: _____

PUMP NO. (not serial) _____

STEL: 1 litre/minute

TWA: 50 cc/minute

STUDY OF EXPOSURE TO MOTOR GASOLINE HYDROCARBONS

ANALYTICAL METHOD

1. When the samples were received at the laboratory, they were logged. The tubes were then broken open, the charcoal separated front and back, and stored in glass vials in a freezer at -20°C.

2. **APPARATUS**

   (a) Hewlett Packard 5890 with a 3392A Integrator, gas chromatograph, autosampler, capillary column and flame ionization detector.

   (b) Column: SPB-1 bonded phase, thick film (1.0um), nonpolar, methyl silicone, fused silica WCOT capillary column (60 m x .32 mm ID).

   (c) Desorbing vials, 1 dram.

   (d) Ultrasonic bath.

   (e) Autosampler vials, 1 ml.

   (f) Syringes of convenient sizes for making standards.

   (g) Pipets, 1.0 ml. type graduated in 0.01 ml increments.

   (h) Volumetric flasks of convenient sizes for making standards.

3. **REAGENTS**

   (a) Spectroquality carbon disfulfide.

   (b) Samples of specific hydrocarbons under study, chromatoquality grade, for use as standards.

   (c) High purity helium.

   (d) High purity hydrogen.

   (e) High purity compressed air.

4. **ANALYSIS OF SAMPLES**

   (a) Desorption of samples. Prior to analysis, 2 ml. of carbon disulfide were pipetted into the vials containing

the charcoal from the samples. The samples were ultrasonicated for at least 30 minutes.

(b) GC conditions. The typical operating conditions for the gas chromatograph were:

(i) 0.6 cc/min. with approximately 30 cc/min. make-up helium carrier gas flow.

(ii) 25.8 cc/min. hydrogen flow.

(iii) 272.7 cc/min. air flow.

(iv) 200°C injection port temperature.

(v) 275°C detector temperature.

(vi) oven temperature program:
32°C for 8 minutes.
180°C at 6°C/min. and held for 5 min.

(c) Each front section was injected twice and each back section was injected once. Approximately 1.4 ml. was injected.

5. DETERMINATION OF DESORPTION EFFICIENCIES

Charcoal tubes from the same lot were scored and opened at the front. The front section was emptied into a 1 dram vial. 2 ml. of a prepared standard was pipetted onto the charcoal. The charcoal was allowed to stand overnight to come to equilibrium. At least three (3) vials were prepared in this manner. These samples in the vials as well as blanks were analyzed in the same manner as the regular samples.

$$\text{Desorption efficiency} = \frac{\text{Sample Concentration - Blank Concentration}}{\text{Concentration of Standard}}$$

This was done for all 55 components; the 56th component being Total Hydrocarbon, determined on the basis of n-hexane. Desorbtion efficiencies are attached.

6. CALIBRATION AND STANDARDS

20 micro-liters of each standard component were injected into 10 ml. of methanol. The exact amount of standard added was calculated by weighing on a semi-micro balance. The stock solution was diluted down again in order to calibrate the gas chromatograph.

All 55 components were calibrated before the analysis of a set of samples.